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THE ROLE OF REFRIGERANT MIXTURES
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The primary approach industry has taken to fill the void resulting from the elimination of the most important CFCs (i.e., R11 and R12) has been to develop other single component refrigerants (i.e., HCFC-123 and HFC-134a) which have very low or zero ozone depletion potential. These alternatives were attractive mostly because they had similar pressure-temperature profiles relative to that which they were replacing and, thus, required minimal machinery design changes for adoption.

No such single component alternative has been discovered for HCFC-22 or R502. As a result, the industry, with its need to meet the various phase-out dates internationally agreed upon, has begun an intensive effort to adapt various zeotropes (nonazeotropes) and, whenever possible, azeotropes to act as "drop-in" alternatives in existing equipment as well as the long term working fluids for new equipment. (Actually no chlorine-free refrigerant can be a true drop-in since a new lubricant is required.)

Concern for the zeotrope's major disadvantage, that of unknown and unwanted composition shifting during leaking and charging situations, has caused the industry to focus only on those zeotropes with minimal temperature and composition changes or glides during phase change. These minimal glide zeotropes have become known as "near-azeotropes" and behave in an "azeotrope-like" manner. Although no formal definition of "near-azeotrope" has been quantified, sufficient research has been conducted to know that a temperature glide greater than 1°C will have a negative effect on the performance of a flooded shell and tube chiller. On the other hand, the true zeotropic benefits (i.e. Lorenz cycle glide matching through counter or cross-counter flow heat exchange) are usually not significant enough to redesign the system unless the glide is of the order of 5°C or more. Thus, the boundary between near-azeotropes and zeotropes is probably between these two temperatures, depending on the system and application. The most important mixtures currently being evaluated by the refrigeration machinery manufacturers are listed in Table 1.

All mixtures offer the advantage that it is possible to have a nonflammable mixture while using a flammable component. To achieve this, it is only necessary to maintain the mixture's composition such that the total amount of flammable component is less than that quantity that would be flammable in air. For some mixtures even this amount may be exceeded since there appears to be some flame quenching effect with some of the chlorine-free non-flammable components that are being considered. Thus, the use of limited amounts of the fluids HFC-32 and HFC-143a, each of which have rather desirable thermodynamic properties, has been made possible. Such developments and terminology have led to both considerable opportunities and misunderstandings and so it is important to review the fundamentals of mixtures.

Table 1 : Examples of Chlorine-Free Mixture alternatives

	Possible alternatives for HCFC-22	(% weight)	Temp. glide at atmos. pressure	Possible alternative for R502	(% weight)	Temp. glide at atmos. pressure
azeotropes	HFC-32/125	50/50	< 0.1°C	HFC - 125/143a	50/50	0.0°C
zeotropes				HFC - 32/125/143a	(10/45/45)	0.5 °C
low glide				HFC - 125/143a/134a	(44/52/4)	0.8 °C
high glide	HFC - 32/125/134a	(10/70/20) (23/25/52) (30/10/60)	4.1°C 7.1°C 7.4°C	HFC - 32/125/134a	(10/70/20) (20/40/40)	4.1°C 6.4°C
	HFC - 32/134a	(30/70)	7.4°C			

T glide = (T dew - T bubble) at atmos. pressure as predicted by REFPROP 4.0

1 Azeotropes

An azeotrope is a mixture of fluids which has the same composition in the vapor phase and liquid phase, when in equilibrium. A binary azeotropic mixture is relatively unusual and a ternary or higher order azeotrope is rare indeed. In the past, at least seven binary azeotropes formed by halogenated hydrocarbons have been developed to the stage of commercialization in refrigeration machinery and at least three (i.e., R500, R502, R503) are still in use. Several others are known but are of no particular advantage. Recently, two new azeotropes, noted in Table 1, have been developed as possible alternatives to HCFC-22 and R502, respectively.

The phase diagram of HFC-125/143a is shown in Figure 1 for various pressure levels. Several characteristics unique to all azeotropes are illustrated.

The mixture's vapor pressure at the azeotropic point must be either lower or higher than that of either of the components. In this case, it is a minimum pressure azeotrope. Thus, on a temperature-composition chart, as shown in the Figure 1, the azeotrope would be at the maximum temperature point. (It is much more common to find a mixture that is a maximum pressure azeotrope such as HFC-32/125).

Another characteristic is that as the operation pressure is increased the azeotropic point will be monotonically shifted in one compositional direction or the other, to eventual non-existence. Figure 1 shows that at a pressure of 2.0 MPa the azeotrope has ceased to exist.

It should also be noted that for any given pressure condition some temperature glide (and thus composition glide) does exist for the phase change processes away from the azeotropic point or region. For the case of the binary halogenated ethanes shown in Figure 1 this glide is so small ($<0.1^{\circ}\text{C}$) everywhere that it can not be graphically seen. For such a binary mixture, there are no significant composition shifting consequences from a thermodynamic performance viewpoint whether the composition in use is at the azeotropic point or not. Nor will the composition of this mixture shift significantly in use in a temperature range above its azeotropic regime, which is where it would normally be applied. This is because the components' normal boiling points are only one degree apart. However, since HFC-143a is flammable, one must be careful to confirm that the slight composition shifting that does occur does not cause the mixture to drift into the flammable regime, since rigorously the "azeotrope" has now become a very "near-azeotrope". A similar, very narrow composition shift behavior pattern exists for the HFC-32/125 azeotrope even though it too loses its azeotropic point in the region of application.

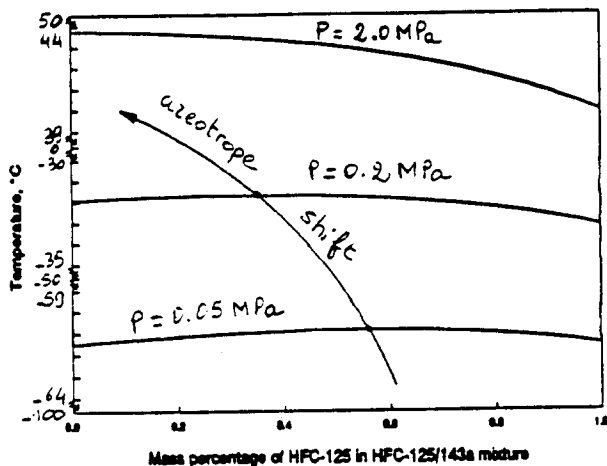


Figure 1

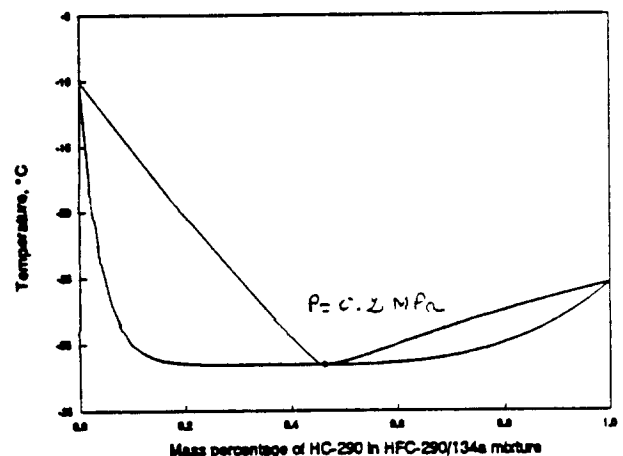


Figure 2

Whereas the HCFC-22 alternatives that are near-azeotropes or zeotropes tend to have vapor pressures similar enough that they may act as drop-ins for some applications, the HFC-32/125 maximum pressure azeotrope has a vapor pressure considerably higher than that of HFC-32, let alone HCFC-22 (see Figure 3). This offers the machinery manufacturers the opportunity to see if the economic trade-offs of higher pressure containment, with its increased wall thicknesses and stronger sealant requirements, are offset by the smaller volumetric capacity requirements and/or the possibility of increased efficiency.

All azeotropes are not necessarily so uniform in composition under different operating conditions. Figure 2 is a phase diagram of an azeotrope between a hydrocarbon (HC-290) and a halogenated hydrocarbon (HFC-134a), which represents an opposite extreme. Here all of the same azeotropic characteristics are in existence but to a different quantitative degree. This azeotrope exists throughout the usual temperature range of application, however, moderate deviations from the azeotropic composition point will result in wide temperature/composition glides which may lead to poor performance, difficulties of field charging procedures, or safety problems.

Whereas, in the past, the ASHRAE 500 series azeotropes were of the first type (that is, of very narrow glides away from the azeotropic point) this may not necessarily be true in the future. One must be careful to understand the full characterization of any new "azeotrope", in particular, in the temperature/pressure range of intended application. In practice, all azeotropes will operate in a nonazeotropic regime which may or may not be of practical significance from a composition glide viewpoint, as well as a safety (i.e., flammability) viewpoint.

II Near-Azeotropes and Zeotropes

Near-azeotropes are zeotropes with minimal temperature and composition glides. No quantification of these minimal glides has been established for definition of the term near-azeotrope, but it is safe to say that what is desired is that there would be little mixture performance change after several half charge losses with original composition recharges. Thus, a near-azeotrope should permit service practices similar to those of azeotropes without a significant effect on system performance and operation.

Unlike azeotropes, all zeotropes (including near-azeotropes) have vapor pressure between that of its components. As seen in Figure 3, the mixture does not have its liquid and vapor saturation lines projected behind one another in the P-T plane as do azeotropes and single component refrigerants. Rather both the bubble and dew lines appears separately as dictated by the temperature glide during the phase change. For the HFC-32/134a (30/70% wt.) shown in Figure 3, the phase lines straddle that of HCFC-22 which suggests a near optimum simulation. Changing the composition or adding other components (e.g., HFC-125) can bring the phase lines closer together (i.e., reduce glide) or move them up or down the pressure scale to change thermodynamic performance. Such is the intent of the ternaries listed in Table 1 as alternatives to HCFC-22. Similarly the R502 alternative possibilities include a binary azeotrope and several ternary near-azeotropes and zeotropes.

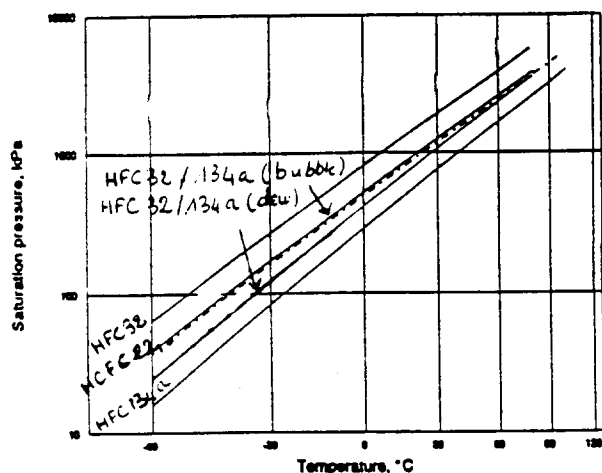


Figure 3

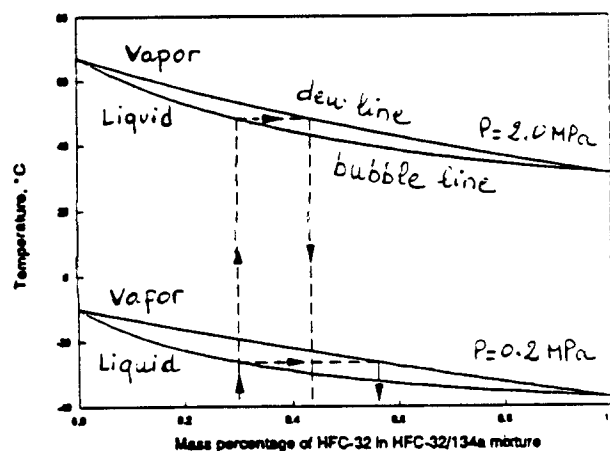


Figure 4

Establishing flammable composition limits for a mixture is complicated by the fact that under the flashing phenomena that container leak conditions would cause, the leaking vapor will generally contain a higher percentage of the more volatile component. The mixture HFC-32/134a is illustrated in Figure 4. Although the initial mixture charge has 30% HFC-32, if it were to leak at a typical condenser pressure ($P=2.0$ MPa), the leaking vapor would contain in excess of 40% HFC-32. Since all mixture phase change envelopes widen as pressure is reduced, this same vapor composition would be over 55 percent HFC-32 in an evaporator leak ($P = 0.2$ MPa). This latter percentage is the beginning flammable range of this mixture in air. For this reason, ASHRAE is currently requiring a "worst case composition shift" scenario to establish the composition to be tested for flammability classification.

The use of a third component can help mitigate this composition shift towards the flammable region in either of two ways. It is possible to surround the flammable component with a more volatile component and one of lower volatility, as is the case of the ternary HFC-125/143a/134a. Or, it is possible to have a substantial quantity of a non flammable component of a similar boiling point as the flammable component, as in HFC-32/125/134a. This concept was at least one of the factors considered in the design of these ternaries.

The flammability issue has been complicated further by continuing development of the test procedure itself (ASTM E-681) and ASHRAE is currently classifying refrigerants under conditions defined in its Standard 34-1993. However, questions have been raised by laboratory differences in test conditions (e.g., test gas temperature, humidity, etc.) and the definition of flammability (e.g., chamber pressure rise versus observation of flame propagation) such that improvements in the procedure are under consideration. Different interpretations of test results have led to a Japanese consensus that HFC-32/134a (30/70 % wt.) is sufficiently safe for use but an American consensus that it is not safe. Continued study of the test procedure and conditions will hopefully bring everyone to agreement.

Theoretically, mixtures with any composition and temperature glide offer the potential for energy savings and capacity control if the machinery system is designed to take advantage of these working fluid attributes. As drop-ins, however, negative performance effects can occur, usually in the heat exchangers due to glide mismatches and/or reduction in refrigerant heat transfer coefficient. How significant these effects are, depends largely on system design and application. Minor alterations, such as changing an indoor cross-flow coil of a split-system air conditioner to cross-counter flow coil can change the same mixture's attribute from a negative to a positive performance factor. With some of the fluids listed in Table 1, this change alone has made the difference between the alternative's performance being less or more efficient than the fluid it was replacing. So here again machinery designers are offered the opportunity to determine which cost effective hardware changes are needed to optimize the new zeotropic alternatives performance.

With the continuing environmental problems the global community faces, the zeotropic working fluids, of even wider glides, continue to offer energy saving opportunities that must be investigated. Progress in this field is best discussed in a more extensive format.